The Radiating Potentials of Nitrogen

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The Radiating Potentials of Nitrogen

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

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THE RADIATING POTENTIALS OF NITROGEN.

BY H. D. SMYTH.

SYNOPSIS.

1. A formula is derived by which accurate corrections allowing for the distribution of velocities of the impacting electrons may be applied to the observed values of the radiating potentials.

2. Measurements on nitrogen revealed—

(*a*) a very strong effect at 8.29 ± 0.04 volts.

(*b*) a very doubtful effect at 7.3 volts.

(*c*) an effect appearing only at lower pressures but strongly at 6.29 ± .06 volts.

3. These results are explained as follows:

(*a*) The wave-length λ corresponding to 8.29 ± .04 is 1490.7 ± 10 and this effect is ,therefore, identified with the doublet found by Lyman at 1492.8 and 1494.8.

(*b*) This gives λ = 1700 and may be identified with the second doublet 1742.7 and 1745.3 attributed to nitrogen but by some thought due to silicon.

(*c*) The value λ = 1965 ± 20 from 6.29 ± .06 volts is taken to correspond to the beginning of the band spectrum at 1870.9. The discrepancy is attributed to the presence of nitrous oxide.

According to another theory the effect at 6.29 is considered due to lines in the region 2,000–3,000 A.U. coming from neutral atoms. The value 6.29 in this case is taken as the speed necessary before the electrons can split up the molecules.

4. From 3 (*a*) assuming line spectra to come from atoms, we have as an upper limit to the heat of dissociation of a gram molecule of nitrogen 190,000 calories.

From the second theory in 3 (*b*) we have as a possoible actual value for this heat of dissociation 145,000 calories.

5. Qualitative evidence was obtained supporting Davis and Goucher's discovery of true ionization in the neighborhood of 18 volts.

I. INTRODUCTION.

THE substances whose minimum radiating and ionizing potentials have been investigated fall naturally into two classes, first, the monatomic gases and metallic vapors, in which collisions below a certain velocity are elastic, and second, the diatomic gases, in which collisions at all velocities are inelastic or at least partially so, as in the case of hydrogen.

The investigations for substances of the first class have recently been summarized and discussed by McClennan.[1] The conclusions drawn are, briefly, as follows. A vapor, when bombarded by electrons of velocity V emits a radiation $eV = h\nu$. The first radiation produced is the line

[1] J. C. McClennan, "The Origin of Spectra," Proc. London Phys. Soc., XXXI., Part I., pp. 1–29, 1918.

at the head of the single t principal series, and thereafter shorter and shorter wave-length radiations set in as the bombarding electrons attain correspondingly higher velocities. Finally, when the speed of the electrons reaches a value corresponding to the frequency $\nu = (1.5, S)$, the convergence frequency of the singlet principal series of the element in question, ionization occurs.

For diatomic gases the mechanism of ionization or the production of radiation is obviously more complicated than where only a single atom is involved. Either it is necessary first to dissociate the molecules and then, by a second impact, to cause radiation or ionization, or only one collision is necessary. Again, if the effect is the result of one impact, it may occur in two ways; an electron may be displaced and the molecule broken up simultaneously, or an electron may be displaced without affecting the bond between the atoms.

Possibly as a result of the above, the spectra of the diatomic gases are very complex and, for the most part, not resolved into series. This makes the prediction of ionizing and radiating potentials difficult. Another source of error especially serious in the case of diatomic gases arises from the uncertainty in applying the necessary correction for velocity distribution, as discussed later in the paper.

In consequence of these complications, although values of the ionizing and radiating potentials have been determined for a number of different diatomic elements and compounds, little has been accomplished toward connecting them with the spectra. In spite of the simple structure of the hydrogen molecule and the extensive data on the spectrum available, the experimental results obtained have not yet been reconciled with those predicted by Bohr's theory or by the quantum relation[1] $eV = h\nu$.

Though the spectrum of nitrogen has not been resolved into series, in the region of the ultra-violet with which we are concerned the line spectrum is very simple. Lyman,[2] in his investigation of the extreme ultra-violet, found for nitrogen no lines except two doublets, one consisting of the lines 1492.8 and 1494.8 and the other[3] of the lines 1742.7 and 1745.3. Applying the quantum relation to these, we have for the corresponding radiating potentials, 8.28 and 8.27, and 7.04 and 7.08 volts. The longest wave-length of the band spectrum which Lyman found in this region is 1870.9 corresponding to 6.6 volts. Now the generally accepted value for the radiating potential of nitrogen is 7.5

[1] Bergen Davis and F. S. Goucher, PHYS. REV., No. 10, p. 101, 1917.

[2] Lyman, "Spectroscopy of Extreme Ultraviolet," p. 113, 1914.

[3] Possibly due to silicon.

volts while Davis and Goucher[1] found a second more intense radiation at 9 volts.[2]

In view of the discrepancy between these experimental values and those calculated from the spectrum, it was thought worth while to attempt a more exact determination.

II. Apparatus.

The apparatus used had been designed for a somewhat different purpose but was found fairly satisfactory.

As shown in Fig. 1, it consisted of a glass tube 1.5″ in diameter, with a filament *F* sealed in at one end, a gauze *G* in the middle and a disc *P* sealed in from the other end, all of platinum. Electrical connections

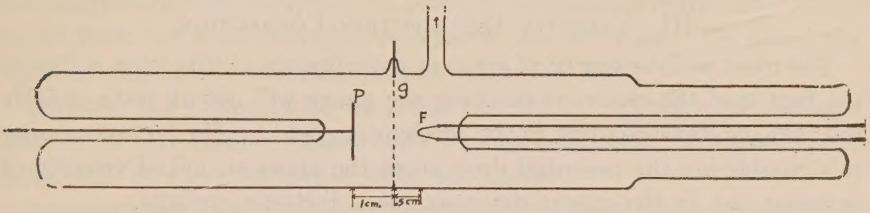

Fig. 1.

were so arranged that the electrons coming off from the hot filament *F* were accelerated by a field between *F* and *G* but met a stronger retarding field between *G* and *P*. The difference between accelerating and retarding fields remained constant. The gauze *G* was connected to a Leeds & Northrup high sensitivity galvanometer which measured the electronic current between *F* and *G*. The disc *P* was connected to a Dolazalek electrometer of sensitivity about 3,000 millimeters per volt, making the capacity of the electrometer system of the order of magnitude of 50 cm. The potentials were read on a Robt. W. Paul voltmeter.

By coating the filament with barium oxide increased emission was obtained.

The pressure in the apparatus was regulated by a Gaede pump and measured with a McLeod gauge.

Nitrogen was prepared by heating sodium nitrite and ammonium chloride with distilled water and was introduced through a drying tube. The apparatus was evacuated and washed out several times with nitrogen before measurements were made.

The setting in of radiation was detected in the usual manner by the photoelectric effect on *P* causing an increase in the speed of deflection of

[1] Bergen Davis and F. S. Goucher, Phys. Rev., No. 13, pp. 1–5, 1919.

[2] The fact that these are radiation effects and not ionization seems to have been proved by Davis and Goucher and is taken for granted in this paper.

the electrometer. It was found impossible to eliminate all zero drift from the electrometer. This made it necessary to start readings far enough below the break point to give a good zero. The accelerating potential was run from 3 or 4 volts up to 11 or 12 and then down again, the intervals between readings near critical points being as small as .2 of a volt. The values going up and coming back were averaged. The electronic current measured by the galvanometer was kept constant in the earlier runs by adjusting the temperature of the filament but, in the later runs, the temperature of the filament was maintained constant and the galvanometer current allowed to vary with the accelerating potential, thus tending to accentuate the sharpness of the break.

III. Velocity Distribution Correction.

The most serious source of error in experiments of this type is due to the fact that the electrons reaching the gauze will not all have exactly the velocity corresponding to the accelerating field.[1] The factors causing this trouble are the potential drop along the filament, initial velocity of emission and, in the case of diatomic gases, inelastic impacts.

Now, in the case of monatomic gases the elastic impacts make possible a very effective method of eliminating this error. In this case, the electrometer current rises rapidly as the accelerating field passes the critical value, reaching a maximum when all the electrons have attained the critical speed, and then falls off again as more and more of the ionizing collisions take place on the filament side of the gauze. When the accelerating potential becomes great enough to allow two ionizing collisions by one electron another maximum occurs, and so on. Thus, by measuring the intervals between successive maxima the true value of the ionizing potential can be found.[2]

With diatomic gases, however, this method is impossible since, with every increase of the accelerating field, some electrons which have lost energy by inelastic impact will attain the critical speed and there will be a continuous increase in the electrometer current. It becomes necessary, therefore, to actually measure the velocity of the electrons coming across and then make a correction.

Franck and Hertz did this but felt so uncertain as to the right method of making the correction that they claimed an accuracy of only one volt[3] for their results.

Goucher[4] eliminated errors due to the potential drop along the filament

[1] J. Franck and G. Hertz, Verh. d. D. Phys. Ges., 15, p. 37, 1913.

[2] J. Franck and G. Hertz, Verh. d. D. Phys. Ges., 16, p. 457, 1914.

[3] J. Franck and G. Hertz, Verh. d. D. Phys. Ges., 15, p. 39, 1913.

[4] F. S. Goucher, PHYS. REV., No. 8, p. 561, 1916.

by introducing an equipotential electron source consisting of a platinum thimble surrounding a tungsten heating element. With this arrangement in mercury vapor he found that over 70 per cent. of the electrons had velocities corresponding to the applied voltage and, further, that the number having a velocity corresponding to .5 volt greater than the applied field was too small to be measured. He therefore made no correction for velocity distribution. In the later work of Davis and Goucher[1] on nitrogen, the same type of electron source was used and the correction considered unnecessary. As before stated the values obtained were 7.5 and 9 volts.

Bishop,[2] working with a filament, took the point of maximum slope of his electron current curve for his velocity distribution correction. That is, he took the most probable velocity of the electrons. He found the value of 7.5 volts for nitrogen and the same for N_2O.

Hughes and Dixon,[3] who obtained the values 7.7 volts for nitrogen and 9.3 for nitric oxide, took as their velocity correction the highest speed detectable on their velocity distribution curve.

Attempts to apply velocity distribution corrections in preliminary tests of the present apparatus proved that the methods mentioned above give quite different results, and that the discrepancy between them varies with the filament temperature and gas pressure. Furthermore, when correcting by the method of Hughes and Dixon, the relative sensitivities of the apparatus for radiation and for velocity distribution measurements and, also, the scale to which the measurements were plotted could be altered so as to vary the value of the corrected "break" point by as much as a volt, without any obvious way of selecting the correct value from among the various possible ones.

This experience led to a closer study of the problem with a view of determining the method of handling data from the two types of measurement which would give the most nearly correct result. The variation of zero drift sets a practical limit to the scale of plotting of either curve. Therefore, it remains to determine an appropriate scale for the more sensitive measurement and this is done by finding the relation between the sensitivities of the apparatus for the two types of measurement. Obviously, the "break" point in the radiation curve is due to the radiation from the smallest number of electrons which can produce a large enough radiation effect to be detected by the apparatus. Since not all electrons capable of producing radiation do so, owing to failure to collide or for other reasons, this "smallest" number of electrons is larger than

[1] Bergen Davis and F. S. Goucher, PHYS. REV., No. 13, p. 1, 1919.

[2] F. M. Bishop, PHYS. REV., No. 10, p. 244, 1917.

[3] A. Ll. Hughes and A. A. Dixon, PHYS. REV., No. 10, p. 495, 1917.

the least number which can be detected if they are permitted to strike the receiving electrode, as in the velocity distribution measurements. The problem, therefore, is to find how many electrons must pass the gauze with sufficient energy to cause radiation in order that one may produce radiation. In other words, how many times less sensitive is the apparatus for radiation than for velocity distribution measurements and how should the latter be plotted in order that the greatest velocity shown should give the correction appropriate to the "break" point in the former?

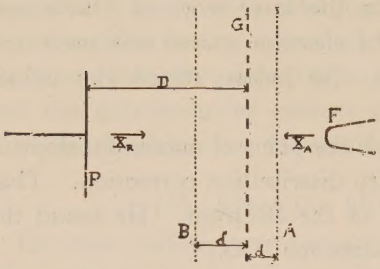

Fig. 2.

The following analysis leads to a very usable expression for the ratio of the sensitivity of the electrometer system for radiation to that for velocity distribution experiments.

Let:

N = number of collisions per centimeter path at 1 mm. pressure;

X_A and X_R = the electric intensities in the accelerating and retarding fields, respectively;

n = number of electrons per unit time reaching the gauze G from the filament side;

$f(V)dV$ = the probability of an electron reaching the gauze with a speed between V and $V + dV$;

V_0 = the minimum radiating velocity;

A and B be two planes parallel to G distant d and d' on either side of it, where

$$d = \frac{V - V_0}{X_A}$$

and

$$d' = \frac{V - V_0}{X_R};$$

$f(V_0)dV$ = the probability of an electron reaching A with velocity between V_0 and $V_0 + dV$.

In all cases, velocities are expressed in terms of equivalent volts.

Evidently

$$nf(V_0)dV(1 - \epsilon^{-pNd}) = n(\epsilon^{pNd} - 1)f(V)dV$$

is the number of electrons which pass A with velocities between V_0 and $V_0 + dV$ and collide before reaching G.

After passing the gauze the electrons will go a distance

$$d' = (V - V_0)/X_R$$

before losing their ability to cause radiation. From these we have

$$nf(V)dV(1 - \epsilon^{-pNd'})$$

as the number of radiating impacts after passing the gauze by electrons which reached the gauze with speeds between V and $V + dV$.

We have, then, for the total number of impacts at a speed greater than V_0, by electrons going in the direction away from the filament,

$$M_1 = n\int_{V_0}^{V_m} (\epsilon^{pN\frac{V-V_0}{X_A}} - \epsilon^{-pN\frac{V-V_0}{X_R}})f(V)dV, \qquad (1)$$

where V_m is the maximum speed of any electron reaching G.

There will also be a small number of electrons which will go through, be stopped, and acquire sufficient acceleration in the opposite direction to produce radiation. For these we have

$$n' = n\epsilon^{-pN\left(\frac{V-V_0}{X_R}\right)}f(V)dV$$

as the number which do not collide before their velocity is retarded to V_0, and

$$n'' = n'\epsilon^{-pN\frac{2V_0}{X_R}}$$

as the number which will regain a velocity V_0 in the opposite direction before collision.

Then

$$n''(1 - \epsilon^{-pN(d'+d)})$$

is the number which, having passed G with velocity between V and $V + dV$, escape collision until they have reversed their direction and regained a speed greater than V_0, finally colliding before their speed is again reduced to V_0.

On substitution we have

$$\begin{aligned} dM_2 &= n'\epsilon^{-pN\frac{2V_0}{X_R}}(1 - \epsilon^{-pN(d'+d)}) \\ &= n\epsilon^{-pN\frac{2V_0}{X_R}}\cdot\epsilon^{-pN\left(\frac{V-V_0}{X_R}\right)}[1 - \epsilon^{-pN\left(\frac{V-V_0}{X_R}+\frac{V-V_0}{X_A}\right)}]f(V)dV \qquad (2) \\ &= n[\epsilon^{-pN\frac{V+V_0}{X_R}} - \epsilon^{-pN\left(\frac{2V}{X_R}+\frac{V-V_0}{X_A}\right)}]f(V)dV. \end{aligned}$$

Therefore

$$M_2 = n\int_{V_0}^{V_m} [\epsilon^{-pN\frac{V+V_0}{X_R}} - \epsilon^{-pN\left(\frac{2V}{X_R}+\frac{V-V_0}{X_A}\right)}]f(V)dV \qquad (3)$$

is the number of collisions by electrons coming in the reverse direction and colliding while they have a velocity between V_m and V_0.

We have, for the total number of collisions by electrons having velocities greater than V_0,

$$M = n\int_{V_0}^{V_m}[\epsilon^{pN\frac{V-V_0}{X_A}} - \epsilon^{-pN\frac{V-V_0}{X_R}}]f(V)dV + n\int_{V_0}^{V_m}[\epsilon^{-pN\frac{V+V_0}{X_R}} - \epsilon^{-pN\left(\frac{2V}{X_R}+\frac{V-V_0}{X_A}\right)}]f(V)dV. \quad (4)$$

Now if we take the probability of the production of radiation and its detection by photoelectric effect to be $(V - V_0)/kV_0$, where the value of kV_0 may be found from the results of Johnson[1] we have for the effective number of radiating impacts when the maximum electronic speed is V_m,

$$M' = n\int_{V_0}^{V_m}\frac{V-V_0}{kV_0}[\epsilon^{pN\frac{V-V_0}{X_A}} - \epsilon^{-pN\frac{V-V_0}{X_R}}]f(V)dV + n\int_{V_0}^{V_m}\frac{V-V_0}{kV_0}[\epsilon^{-pN\frac{V+V_0}{X_R}} - \epsilon^{-pN\left(\frac{2V}{X_R}+\frac{V-V_0}{X_A}\right)}]f(V)dV. \quad (5)$$

We now turn to the velocity distribution measurements. If D is the distance from the gauze G to the plate P and V_R is the retarding potential, the number of electrons getting to the plate will be, for given values of V_m (*i.e.*, V_A, the accelerating potential) and V_R,

$$M_P = n\int_{V_R}^{V_m}\epsilon^{-pND}f(V)dV. \quad (6)$$

Now, the form of the function $f(V)$ will vary with V_m (or V_A) and its value will depend also on the particular value of V substituted.

For a given value of V_m we will have, from (6),

$$\frac{dM_P}{dV_R} = -n\epsilon^{-pND}f(V)_{V=V_R}. \quad (7)$$

Consider the part near the foot of a typical velocity distribution curve, as shown by Fig. 3. The curve is a section of a parabola, while actual experimental measurements are indicated by dots. It is evidently sufficiently accurate, for the present purposes, to consider the lowest part of the distribution curve to be parabolic, so that its slope is taken to be proportional to the horizontal distance from the foot. Use of this property gives the graph shown in Fig. 4.

Let $V_{R'}$ be some particular value of V_R; then

$$(M_P)_{V_R=V_{R'}} = -\tfrac{1}{2}(V_m - V_{R'})\left(\frac{dM_P}{dV_R}\right)_{V_R=V_{R'}}.$$

Also, we have, for any value of V_R less than V_m,

$$\frac{dM_P}{dV_R} = \frac{V_m - V_R}{V_m - V_{R'}}\left(\frac{dM_P}{dV_R}\right)_{V_R=V_{R'}}.$$

[1] J. B. Johnson, PHYS. REV., X., p. 609, 1917.

Combining these two equations, we have

$$(M_P)_{V_{R'}} = -\frac{1}{2}\frac{(V_m - V_{R'})^2}{V_m - V_R}\frac{dM_P}{dV_R}.$$

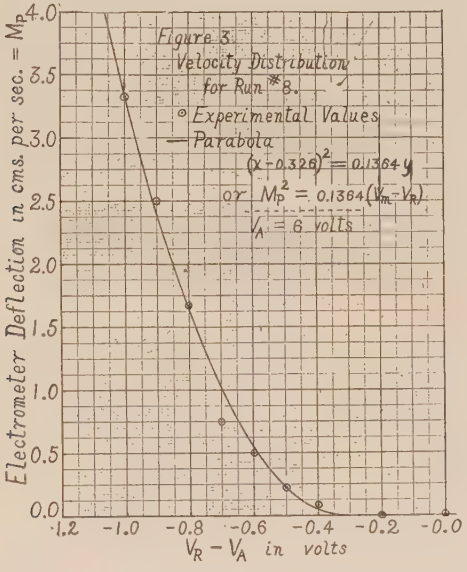

Fig. 3.

Substituting for dM_P/dV_R from (7), and solving for $f(V)_{V=V_R}$, we have

$$f(V)_{V=V_R} = \frac{2(M_P)_{V_{R'}}(V_m - V_R)\epsilon^{pND}}{n(V_m - V_{R'})^2}.$$

We are endeavoring to find the ratio of corresponding values of M'

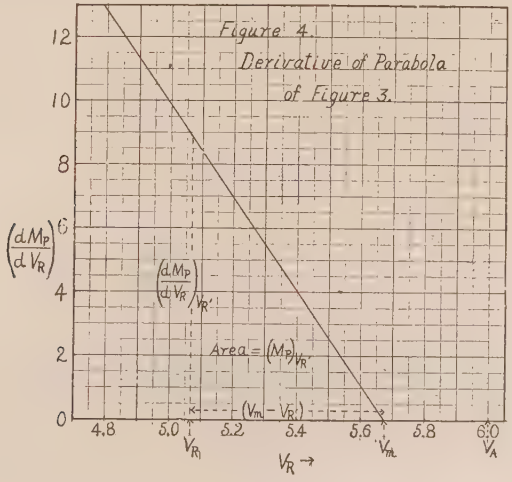

Fig. 4.

and M_P, *i.e.*, of values at equal distances from the break point. For this condition we must have

$$V_m - V_0 = V_m - V_{R'}$$

and $(V - V_0)$ in the case of radiation corresponds to $(V_m - V_R)$ in the velocity distribution. We can therefore substitute the value found above for $f(V)$ in the expression for M' if we write $V_m - V_0$ for $V_m - V_R$ and $V - V_0$ for $V_m - V_R$. If at the same time we divide through by $(M_P)_{V_{R'}}$, we have the following expression for the required ratio:

$$\frac{M'}{M_P} = 2\epsilon^{pND}\int_{V_0}^{V_m} \frac{1}{(V_m - V_0)^2}\frac{(V - V_0)^2}{kV_0}[\epsilon^{pN\frac{V-V_0}{X_A}} - \epsilon^{-pN\frac{V-V_0}{X_R}} + \epsilon^{-pN\frac{V+V_0}{X_R}} - \epsilon^{-pN\left(\frac{2V}{X_R}+\frac{V-V_0}{X_A}\right)}]dV$$

for corresponding values of M' and M_P in the neighborhood of the break point.

If, in the above expression, we put the constant factors outside the integral and set $pN/X_A = a$, $pN/X_R = a'$ and $V - V_0 = x$, and if we take $a = a'$, which is very nearly true we have

$$\frac{M'}{M_P} = \frac{2\epsilon^{pND}}{kV_0(V_m - V_0)^2}\int_0^{x_m} x^2[\epsilon^{ax} - \epsilon^{-ax} + \epsilon^{-2aV_0}(\epsilon^{-ax} - \epsilon^{-3ax})]dx.$$

By integration and the expansion of the powers of ϵ (either before or after integration), this equation takes the following form, which includes all terms as far as those in a^3:

$$\frac{M'}{M_P} = \frac{2a\epsilon^{pNL}(V_m - V_0)^2}{kV_0}[1 - aV_0 - \tfrac{4}{5}a(V_m - V_0) + \tfrac{7}{9}a^2(V_m - V_0)^2 + \tfrac{1}{5}\tfrac{6}{}a^2V_0(V_m - V_0) + 2a^2V_0^2 + \cdots].$$

Practically, the terms in a^2 are negligible, since a is of the order of magnitude of 0.03.

If, therefore, we call the sensitivity of the apparatus for radiation R and for velocity distribution S, we have, for practical purposes,

$$\frac{R}{S} = \frac{M'}{10M_m} = \frac{\epsilon^{pND}a(V_m - V_0)^2}{5kV_0}(1 - aV_0) = \frac{\epsilon^{pND}a(V_m - V_R)^2}{5kV_0}(1 - aV_0), \tag{8}$$

where V_m is the maximum speed detectable in velocity distribution measurements and the factor 1/10 is introduced because, in our apparatus, the dimensions were such that P receives only about that proportion of the radiation starting at the gauze.

Equation (8) is evidently not exact, owing to the approximations

introduced in order to obtain a solution. It is believed, however, that none of these approximations is seriously in error, so that the results given by (8) should be of the right order of magnitude.

The necessary procedure, therefore, is to plot the velocity distribution on the same scale on which the radiation curve is to be plotted and determine V_m from this. Then multiply the values of the electrometer current for each value of V_R by the corresponding values of R/S and replot. The break point in this new curve determines the correction to be used on the radiation curve. The necessity of plotting a corrected velocity distribution curve is made evident by Table I. which gives the values of S/R calculated by equation (8) for different values of $V_R - V_m$, taking $k = 2$ for nitrogen.[1]

TABLE I.

$p = 0.015$ mm. $V_0 = 7.5$ volts.

$(V_m - V_R)$.	S/R.	$(V_m - V_R)$.	S/R.
.1	795,000	1.1	6,500
.3	87,500	1.2	5,500
.5	31,000	1.3	4,700
.6	22,000	1.4	4,050
.7	16,000	1.5	3,500
.8	12,500	1.6	3,200
.9	9,500	1.7	2,750
1.0	8,000		

IV. EXPERIMENTAL RESULTS.

It was found impossible to eliminate all zero leak from the electrometer. Consequently readings had to be taken at low accelerating potentials to establish a zero line. Errors due to a variation in this zero leak as well as errors of observation were pretty well eliminated by the method of taking a series of readings with fields increasing and then decreasing and plotting the mean. A typical set of readings is given in Table II., below.

where

V_f = P.D. across filament in volts;

G = current to gauze in amperes $\times 10^{-8}$;

T = time in seconds for electrometer to deflect one cm.;

$\overline{T}$ = mean of T and T' observations as V_A was increased and then decreased respectively;

$1/\overline{T}$ = rate of deflection of electrometer in cms. per second.

The values of V_A and $1/\overline{T}$, that is the accelerating potential and the current to the electrometer, were used in making the curves. The first

[1] J. B. Johnson, *loc. cit.*

TABLE II.

Observations for Run No. 12.

p = 0.01 mm., $V_R - V_A$ = 2.5 volts, V_f = 0.8 volts.

V_A.	G.	G'.	T.	T'.	$\overline{T}$.	$I/\overline{T}$.
1	6	6	81	81	81	.0124
2	16.4	17	79	86	82.5	.0121
3	21.2	21	76	86	81	.0124
4	23	22	82	80	81	.0124
5	23.7	22.4	73	89	81	.0124
5.5	24.1	22.5	71	74	72.5	.0138
5.75	24.4	22.4	76	71	73.5	.0136
6	24.7	22.3	66	61	63.5	.0158
6.25	25	22.1	63	60	61.5	.0163
6.5	25.2	22.1	60	56	58	.0172
6.75	25.5	21.9	55	55.6	55.3	.0181
7	25.8	21.7	50	53	51.5	.0194
7.25	26.2	21.6	46.4	45.4	45.9	.0218
7.5	26.6	21.5	44	44.6	44.3	.0220
7.75	26.9	21.3	41	41	41	.0244
8	27.2	21	35.2	35	35.1	.0285
8.25	27.4	21	29.8	30.2	30	.0330
8.5	27.7	20.9	23.4	27.5	25.5	.0392
8.75	28	20.8	20.2	22.1	21.1	.0474
9	28.2	20.7	16.8	19.4	18.2	.0550
9.5	28.5	20.8	10.6	12.5	11.5	.0870
10	28.7	20.8	7.5	9.0	8.2	.122
11	29.2	21	1.8	3.0	2.4	.417
12	29.5	21.1	.58	.7	.64	1.563

detectable departure from the zero line was taken as the break point. Thus, in run no. 4, Fig. 5, the break point comes at 9.3 volts. In order to correct this we examined the velocity distribution curve for run no. 4 in Fig. 6. Here we saw that the uncorrected values (curve *a*) gave a break point at $V_R - V_A = 0$ and therefore $V_m - V_A = 0$. Using this value to get $(V_m - V_R)$, and so to calculate the corrected values of the current by applying equation 8, we got the curve *b* which has its first break point at $V_R - V_A = -1.0$. We concluded, therefore, that the first electrons which are effective in producing detectable radiation have a velocity one volt less than the applied field, giving us 8.3 as the true value of the radiating potential from this run.

Similarly for run no. 5 we found the observed break to be at 9.0 and the corrected value to be 8.0 volts.

In run no. 6, Fig. 7, on the other hand, we found the corrected value to come at 6.5 (5.9 observed), but there is a sharp increase in the slope

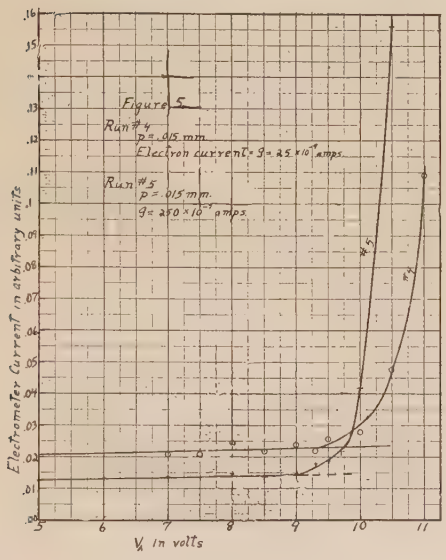

Fig. 5.

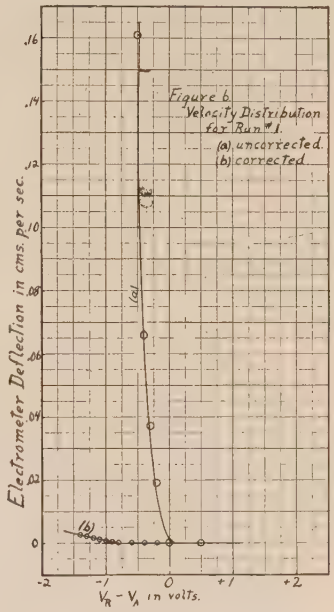

Fig. 6.

of the curve at 8.6 (8.0 observed). This run therefore apparently has two breaks corresponding to two critical speeds.

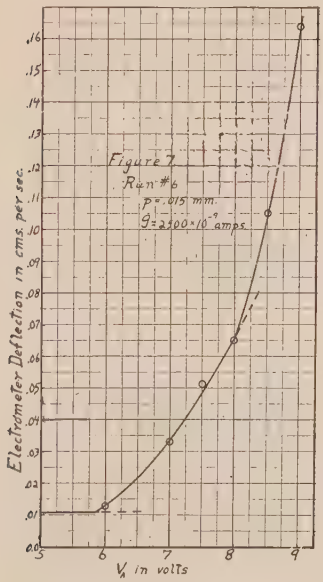

Fig. 7.

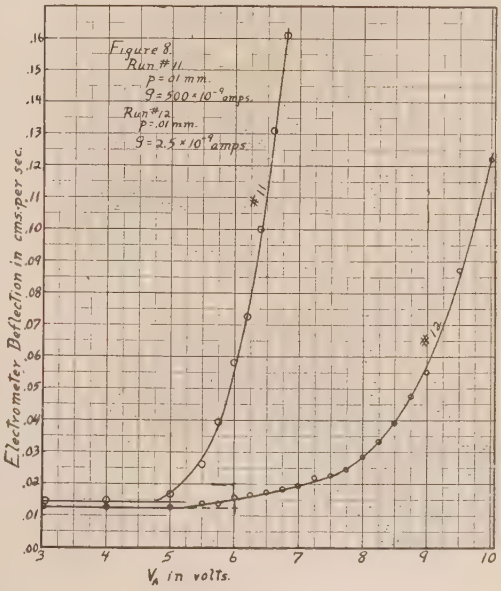

Fig. 8.

In runs nos. 11 and 12 the effect at the lower voltage was so great as to make it impossible to detect any other. For these runs the corrected values are 6.15 and 6.4 volts.

From these five typical curves shown, it is clear there are two distinct critical points, each curve showing one or both more or less sharply. The values observed were weighted according to the sureness with which the break point could be picked. The velocity distribution curves were treated similarly and the weight of the corrected value taken as the product of the weights of the two observations.

In Table III. the results from the curves shown and discussed above are grouped with all other runs which gave results sufficiently definite to have weight.

TABLE III.

Experimental Results.

No.	p (mm.).	G.	Observed Breaks with Weighting.		Corrections with Weighting.	Corrected Breaks with Weighting.	
1	.048	25.	9.4 (4)		−0.4 (3)	8.5 (12)	
2	.038	25.	9.2 (3)		−0.9 (3)	8.3 (9)	
3	.027	25.	9.3 (2)	7.5 (?)	−1.0 (3)	8.3 (6)	
4	,015	25.	9.3 (3)		−1.0 (3)	8.3 (9)	
5	.015	250.	9.0 (4)		−1.0 (3)	8.0 (12)	
6	.015	2500.	8.0 (1)	5.9 (2)	+0.6 (3)	8.6 (3)	6.5 (6)
7	.015	2500.		5.4 (5)	+0.7 (2.5)		6.1 (8)
8	.045	750.	9.3 (2)		−.08 (4)	8.5 (8)	
9	.045	140.	9.2 (1)		−1.0 (4)	8.2 (4)	
10	.026	250.	8.8 (2)	7.4 (1)	−0.7 (5)	8.1 (10)	6.7 (5)
11	.01	500		4.75 (4)	+1.4 (3)		6.15 (12)
12	.01	2.5	7.75 (?)	5.2 (4)	+1.2 (3)		6.4 (12)
13	.01	40	6.5 (?)	4.2 (3)	+1.9 (3)		6.1 (4)
Mean values						8.285 ±.045	6.285 ±.061

Note.—Runs 7, 11 and 13 and some not given above show uncertain indications of a third break at about 7.4 volts; G is the electronic current in amperes $\times 10^{-9}$.

V. DISCUSSION OF RESULTS.

Let us now compare the experimental results just presented with Lyman's data on the spectrum of nitrogen in the extreme ultra-violet given at the beginning of this paper. This is best done by writing corresponding values opposite each other in a table.

1. *The Break at* 8.29 *Volts.*—In this table we see that the effect which we got at all pressures tried and with various currents, that is the most

TABLE IV.

Spectrum Data.			Radiation Experiment Data.	
Remarks.	λ (Obs.).	V_0 (Calc.).	V_0 (Obs.).	λ (Calc.).
Doublet almost certainly due to nitrogen	1492.8 1494.8	8.28 8.27	8.29 ± .04	1490.7 ± 10
Doublet attributed to nitrogen but possibly due to silicon	1742.7 1745.3	7.08 7.09	7.3 (?)	1700 (?)
Beginning of band spectrum	1870.9	6.6	6.29 ± .06	1965 ± 20

intense effect, corresponds with greater accuracy than could be hoped for, to the most certain doublet of the line spectrum of nitrogen.

2. *Possible Effect at 7.3 Volts.*—The failure of the second value to coincide with that for the other doublet is no greater than the uncertainties of its determination. This radiation was apparently the weakest of the three and, while showing up well on one or two curves was, on the whole, rather doubtful. Attention should again be called to the doubt concerning the origin of this doublet as determined by Lyman.

3. *Explanation of 6.29-Volt Break.*—Two different theories were developed to account for this effect, one depending on the application of the quantum relation to the band spectrum and the other involving the idea of dissociation and the subsequent production of spectral lines. They are discussed at length in what follows.

(*a*) To explain the experimental result of a break occurring only at low pressures and coming at 6.29 volts instead of the 6.6 calculated from the band spectrum, we must consider the effect of a probable impurity. Kreusler[1] found that nitrogen prepared in a manner almost identical with that used in the present experiment had a small quantity of N_2O present as an impurity. He found that this increased absorption at λ = 1,860 from 2.2 per cent. for atmospheric nitrogen to 14.3 per cent. He also made measurements on pure nitrous oxide and found 88.4 per cent. absorption at λ = 2,000, apparently increasing beyond his powers of measurement at 1,930 and 1,860.

It is probable, therefore, that at the higher pressures, the radiation λ = 1,965 corresponding to 6.3 volts loses so much energy by absorption in the 1 cm. space between the gauze and the plate that it is not detectable. This explains the fact that there was no trace of this break at pressures above 0.026 and that it was only detected in one case at pressures exceeding 0.015.

[1] H. Kreusler, Ann. d. Phys., 6, p. 419, 1901.

The discrepancy between the value 6.3 found and the 6.6 corresponding to the beginning of the band spectrum is not so easily accounted for. It is a well known fact, however, that the presence of small impurities greatly affects the intensity of emission spectra. We have just seen that there is such an effect in the absorption spectrum of nitrogen in this region. Is it not possible then that the presence of N_2O may cause less refrangible bands up to $\lambda = 1{,}965$ to come out with sufficient strength to be detected? The chances for sufficient experimental error to account for a discrepancy of 0.3 volt do not seem great especially in view of the extremely good agreement in the case of the highest break. It is hoped that this point may be cleared up by further work taking every precaution to get absolutely pure nitrogen.

(*b*) The other explanation of our 6.3 volt break is quite different. There are lines in the spectrum of nitrogen in the region between 2,000 and 3,000 which would produce photoelectric effect and the most refrangible of which is $\lambda = 2{,}052$.[1] In the previous discussion it has been assumed that these arise from systems that are not present in this experiment, such as charged atoms or molecules, since otherwise we would have a photo-electric effect at lower voltages. If we allow the possibility of the production of some of these lines by a neutral atom, as we must for the doublet previously considered, then we must first have dissociation and then a radiating impact. Now the speed necessary for an electron to produce these radiations is between 4 and 6 volts, but the energy necessary to dissociate a nitrogen molecule is unknown. The velocity necessary for an electron to dissociate a hydrogen molecule is found by calculation from Langmuir's[2] results to be about 3.6 volts and it is known that nitrogen is much harder to dissociate. It is possible therefore that 6.3 is the speed necessary to dissociate the molecules and thus make it possible for the electrons of lower speed to produce radiation. This would correspond to a heat of dissociation of a gram molecule of nitrogen of 145,000 calories, whereas Langmuir[3] found for hydrogen the value 84,000.

This theory necessitates a new explanation of the effect of pressure, since these longer wave-length radiations will not be so strongly absorbed. It must be supposed that the chances for recombination of the atoms at higher pressures than 0.026 are so great as to make the radiation negligibly small.

As to the soundness of the assumption of radiation from neutral atoms, we have the following statement of J. J. Thomson regarding the lines of

[1] Lyman, "Spec. of Extreme Ultraviolot," p. 83, 1914.

[2] I. Langmuir, J. of Am. Chem. Soc., 37, pp. 417–458, 1915.

[3] Ibid., p. 457.

the hydrogen spectrum: "All theories concur in regarding the atom and not the molecule as the source of these lines, but according to Wien's theory the atom radiates when in the neutral state, while Stark maintains that the radiation is emitted when the atom has a positive charge: according to his view the lines emitted by the neutral atom are far away in the ultra-violet." [1] Stark[2] found no lines attributable to a neutral nitrogen atom but hardly carried his work below 4,000 A.U. From his work on mercury, however, he concluded that the line 2,536.7 was due to a neutral atom.[3] It is evident then that there is no evidence against our assumption but rather indications of its probability.

A second assumption implied in this theory is that the neutral molecules will not set up ultra-violet radiation when struck by electrons with speeds below 6.3. On this point, I have found no evidence.

4. *Upper Limit to Heat of Dissociation of Nitrogen.*—A necessary consequence of the principle that the line spectrum is due to atomic nitrogen is the determination of an upper limit for the energy necessary to dissociate a nitrogen molecule. If the effect resulting rom bombardment by electrons with velocities of 8.24 volts is due to atoms, the molecules must be dissociated by the impact of electrons of this or lower speed. The value 8.3 would give as an upper limit for the heat of dissociation of a gram molecule of nitrogen about 190,000 calories. As has been stated, Langmuir[4] found the value for hydrogen at constant volume to be 84,000 calories.

VI. Ionization at 18.5 Volts.

Goucher and Davis found that what had previously been called ionization in nitrogen was really radiation but that true ionization did occur at 18.5 volts. Although the apparatus used in the present investigation was not well suited for testing this point, by greatly reducing its sensitivity a distinct increase in the slope of the electrometer current curve in the neighborhood of 18 volts was observed, thus supporting the more accurate work of Davis and Goucher.

It is realized that the present results were not obtained under experimental conditions ideal for getting sharp break points or reducing corrections to a minimum. The attempt was made, on the other hand, to employ experimental conditions in which the corrections would be as varied as possible, in order to test the soundness of the formula.

[1] J. J. Thomson, "Positive Rays," pp. 96–97, 1913.

[2] J. Stark, Ann. d. Phys., 55, pp. 29–74, p. 73, 1914.

[3] J. Stark, Ann. d. Phys., 52, pp. 241–302, p. 247, 1913.

[4] I. Langmuir, *loc. cit.*, p. 457, 1915.

Although the corrections in different tests differed by as much as 3 volts in extreme cases, the corrected values of the break point were quite consistent. It appears, therefore, that the above analysis is justified and necessary, and that the final values obtained are trustworthy.

The author wishes to express his indebtedness to Professor K. T. Compton, whose supervision and assistance have made this work possible.

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